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DE FR GB• Ushio, Yoshito, c/o Dow Corning  
Ichihara-shi, Chiba Pref. (JP)

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(71) Applicant: Dow Corning Toray Silicone Company  
Limited  
Tokyo (JP)(74) Representative: Dowden, Marina  
Elkington and Fife  
Prospect House,  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)(72) Inventors:  
• Nakamura, Akito, c/o Dow Corning  
Ichihara-shi, Chiba Pref. (JP)

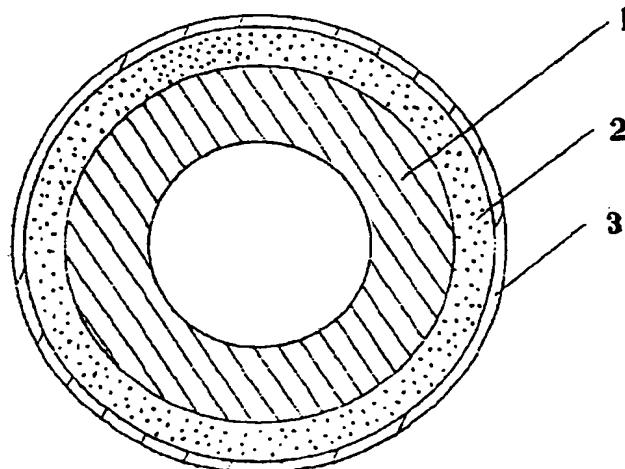
## (54) Silicone rubber composition for fluororesin-covered fixing rolls and fluororesin-covered fixing rolls

(57) Silicone rubber composition comprising an alkenyl-substituted diorganopolysiloxane, an inorganic filler, an organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, in a quantity that affords a value from 0.4 to 10 for the molar ratio of silicon-bonded hydrogen in the organopolysiloxane to alkenyl groups in the alkenyl-substituted diorganopolysiloxane, an organohydrogenpolysiloxane, in a quantity that affords a value from 0.01 to 0.5 for the

molar ratio of silicon-bonded hydrogen in this component to alkenyl groups in the alkenyl-substituted diorganopolysiloxane, and a platinum catalyst.

A fluororesin-covered fixing roll in which a fluororesin layer is placed over the circumference of a roll shaft with a silicone rubber layer interposed between the fluororesin layer and the roll shaft, wherein said silicone rubber composition is formed by curing the silicone rubber composition described above.

Figure 1.



## Description

This invention relates to silicone rubber compositions for use in fluororesin-covered fixing rolls (hereinafter abbreviated as FFRs) and to FFRs themselves. More particularly, this invention introduces an FFR silicone rubber composition that - even when cured at the relatively low temperatures necessary to avoid development of wrinkles or creases in the surface of FFRs - is nevertheless capable of forming a silicone rubber with a low compression set and an excellent adherence to the roll shaft. The invention also provides a highly FFR for use in copier machines.

5 FFRs, comprising a fluororesin layer formed on the circumference of a metal roll shaft across an intercalated layer of relatively low-durometer silicone rubber, exhibit excellent toner release and make possible a reduction in equipment 10 size. Therefore, they are well-adapted for use in electrophotographic copiers, printers, facsimile machines, and the like (refer to JP-As 53-74436, 57-89785, 59-74578 and 59-52269).

15 Typically, FFRs are fabricated by preliminary treating the circumference of the roll shaft with primer, inserting the treated roll shaft into a fluororesin tube; injecting a silicone rubber composition into the cavity created between the roll shaft and the tube, and then curing the silicone rubber composition. This process requires that the silicone rubber 20 composition be cured at relatively high temperatures, for example, at 150°C to 200°C, to achieve a satisfactory adhesion between the roll shaft and the silicone rubber layer. However, due to the difference in coefficients of thermal expansion 25 between the silicone rubber composition and fluororesin, this heating episode frequently causes the appearance of creases or wrinkles in the surface of the resulting fixing roll. This problem is particularly noticeable with the use of silicone rubber compositions that yield low-durometer silicone rubbers, for example, with a JIS A durometer not exceeding 20.

When the silicone rubber composition is cured at relatively low temperatures, for example, 80°C to 120°C which 25 avoid creasing in the surface of the FFR, the result is a poor adherence and intimacy of contact between the roll shaft and fluororesin that are in contact with the silicone rubber composition during its cure. As a consequence, even the preliminary treatment of the roll shaft with a primer does not yield much improvement in adherence. Thus, while FFRs 30 fabricated by a low-temperature cure silicone rubber composition do not suffer from surface creasing, they will suffer from a poor reliability due to a tendency for delamination at the roll shaft/silicone rubber layer interface.

35 As a result of extensive investigations directed to solving the above problems, we unexpectedly found that an addition reaction-curing silicone rubber composition, which contains two different types of SiH-functional organopolysiloxane, can be cured even at relatively low temperatures to yield a silicone rubber with a low compression set and an excellent adherence and intimacy of contact with a roll shaft and fluororesin in contact with the composition during 40 its cure. With respect to these SiH-functional organopolysiloxanes, we discovered in particular that the use of specific quantities of organopolysiloxane containing relatively large amounts of SiH can increase the adherence without significantly changing the physical properties of the silicone rubber product - most importantly without significantly changing its durometer. The present invention was achieved based on these findings.

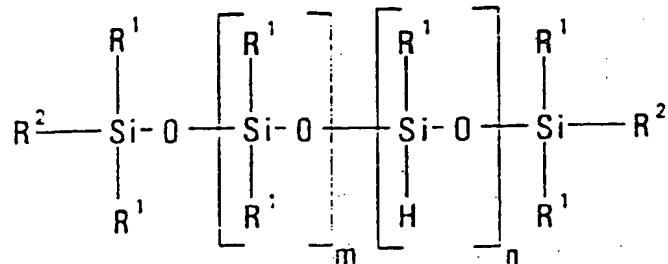
45 The present invention takes as its object the introduction of an FFR silicone rubber composition that - even when cured at the relatively low temperatures necessary to avoid development of creases in the surface of FFRs - will form a relatively low-durometer silicone rubber with a low compression set and an excellent adherence to the roll shaft. Another object of the present invention is to provide highly reliable FFRs.

The silicone rubber composition of the present invention comprises:

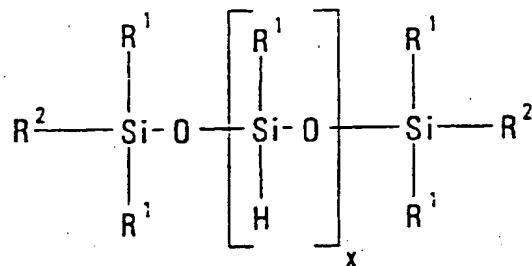
50 (A) 100 parts by weight of a diorganopolysiloxane having an average of at least two silicon-bonded alkenyl groups per molecule and containing an average at least 0.5 silicon-bonded alkenyl groups per molecule in pendant positions on the molecular chain;

(B) 5 to 500 parts by weight of a filler;

55 (C) an organopolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, in a quantity that affords a value from 0.4 to 10 for the molar ratio of silicon-bonded hydrogen in component (C) to alkenyl groups in component (A), said organopolysiloxane having the general formula



(D) an organohydrogenpolysiloxane with the general formula



said organohydrogenpolysiloxane having an average of at least two silicon-bonded hydrogen atoms in each molecule, in a quantity that affords a value from 0.01 to 0.5 for the molar ratio of silicon-bonded hydrogen atoms in component (D) to alkenyl groups in component (A); and  
(E) platinum catalyst in a catalytic quantity;

wherein R<sup>1</sup> is a monovalent hydrocarbon group, R<sup>2</sup> is a hydrogen atom or a monovalent hydrocarbon group, m is a positive integer, n is an integer with a value of zero or greater, x is a positive integer, and both the organopolysiloxane and the organohydrogenpolysiloxane are free of alkenyl groups.

The present invention also provides a FFR having a silicone rubber layer that is formed by curing the above silicone rubber composition described above.

Figure 1 contains a cross section of a fluororesin-covered fixing roll according to the present invention.

The diorganopolysiloxane (A) characteristically contains at least two silicon-bonded alkenyl groups in each molecule and has an average of at least 0.5 silicon-bonded alkenyl group in pendant positions along the molecular chain. Component (A) must contain on average at least 0.5 silicon-bonded alkenyl to obtain a silicone rubber with a low compression set. Component (A) must also contain an average of at least two silicon-bonded alkenyl groups per molecule to achieve a thorough cure of the composition. In preferred embodiments, the silicon-bonded alkenyl in component (A) is selected from the group consisting of vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl. Vinyl is particularly preferred. The non-alkenyl silicon-bonded groups of component (A) are exemplified by alkyl groups, such as methyl, ethyl, propyl, butyl, pentyl, and hexyl; aryl groups such as phenyl, tolyl and xylyl; aralkyl groups such as benzyl or phenethyl; haloalkyl groups such as 3-chloropropyl or 3,3,3-trifluoropropyl; alkoxy groups such as methoxy and ethoxy; and hydroxyl group. The methyl group is specifically preferred among the preceding. The viscosity of component (A) at 25°C is preferably at least 1 000 mPa.s (centipoise), wherein the range from 1,000 to 1,000,000 mPa.s (centipoise) is more preferred and the range from 10,000 to 500,000 mPa.s (centipoise) is most preferred.

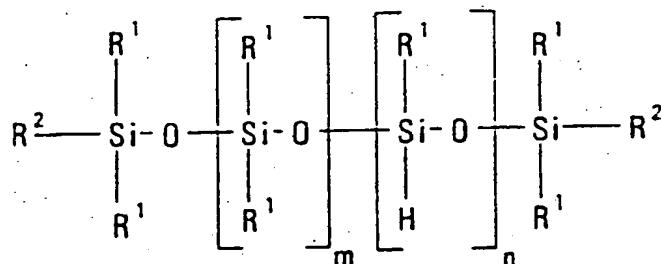
The diorganopolysiloxane (A) is exemplified by trimethylsiloxy-endblocked methylvinylsiloxane - dimethylsiloxane copolymers, trimethylsiloxy-endblocked methylvinylpolysiloxanes, trimethylsiloxy-endblocked methylvinylsiloxane-methylphenylsiloxane copolymers, trimethylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane-methylphenylsiloxane copolymers, trimethylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers, dimethylvinylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane copolymers, dimethylvinylsiloxy-endblocked methylvinylpolysiloxanes, dimethylvinylsiloxy-endblocked methylvinylsiloxane-methylphenylsiloxane copolymers, dimethylvinylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane-methylphenylsiloxane copolymers, silanol-endblocked methylvinylsiloxane-dimethylsiloxane copolymers, silanol-endblocked methylvinylpolysiloxanes, silanol-endblocked methylvinylsiloxane-dimethylsiloxane-methylphenylsiloxane copolymers, and silanol-endblocked methylvinylsiloxane-dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers. These diorganopolysiloxanes may be used singly or in combinations of two or more. A portion of component (A) can be diorganopolysiloxane that does not contain pendant silicon-bonded alkenyl, such as dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethylsiloxane-methylphenylsiloxane copolymers, and dimethylvinylsiloxy-end-blocked dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers.

The inorganic filler (B) imparts properties such as mechanical strength, thermal conductivity, or electrical conductivity to the cured silicone rubber composition. Component (B) is exemplified by precipitated silica, fumed silica, calcined silica, fumed titanium oxide, crushed quartz, diatomaceous earth, aluminosilicate, iron oxide, zinc oxide, calcium carbonate, carbon black, alumina aluminum hydroxide, silver, and nickel. These inorganic fillers may be directly admixed in an untreated form; or they may be admixed after a preliminary surface treatment with an organosilicon compound such as an organoalkoxysilane, organochlorosilane, or organodisilazane; or they may be subjected to surface treatment with such an organosilicon compound while being mixed into component (A).

Component (B) is present at from 5 to 500 weight parts, per 100 weight parts of component (A), and is preferably

admixed at from 10 to 300 weight parts per 100 weight parts component (A). The ultimately obtained silicone rubber will have a poor mechanical strength when component (B) is added at less than 5 weight parts per 100 weight parts of component (A). The silicone rubber composition becomes quite difficult to prepare when more than 500 weight parts of component (B) is used.

5 The organopolysiloxane (C), which functions to cure the present composition, is defined by the following general formula



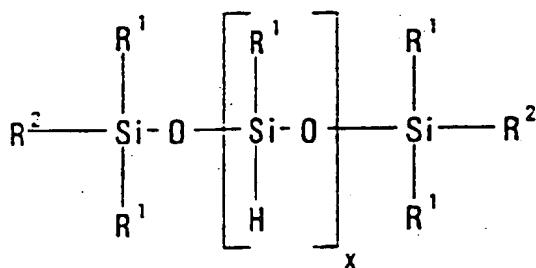
20 and contains an average of at least two silicon-bonded hydrogen atoms per molecule.  $\text{R}^1$  represents monovalent hydrocarbon groups excluding alkenyl groups, and is exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, and hexyl; aryl groups such as phenyl, tolyl and xylyl; aralkyl groups such as benzyl or phenethyl; and haloalkyl groups such as 3-chloropropyl, or 3,3,3-trifluoropropyl. The methyl group is specifically preferred.  $\text{R}^2$  therein represents hydrogen atom and monovalent hydrocarbon groups excluding alkenyl groups. The monovalent hydrocarbon groups are exemplified by the same hydrocarbon groups as above. The subscript  $m$  is a positive integer, while the subscript  $n$  is an integer with a value of 0 or greater. To produce silicone rubbers with a relatively low durometer, e.g., a JIS A durometer of no more than 20, the organopolysiloxane (C) preferably contains 2 to 4 silicon-bonded hydrogen atoms in each molecule. The viscosity of component (C) at 25°C is preferably from 3 to 10,000 mPa.s (centipoise) and more preferably is from 3 to 300 mPa.s (centipoise). The organopolysiloxane (C) is exemplified by dimethylhydrogensiloxo-endblocked dimethylpolysiloxanes, dimethylhydrogensiloxo-endblocked dimethylsiloxane-methylphenylsiloxane copolymers, trimethylsiloxo-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylsiloxane-methylphenylsiloxane-methylhydrogensiloxane copolymers, and dimethylhydrogensiloxo-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers. These organopolysiloxanes may be used singly or as combinations of two or more.

25

30 Component (C) is added in a quantity that affords a value from 0.4 to 10 and preferably from 0.6 to 5 for the molar ratio of silicon-bonded hydrogen atoms in component (C) to alkenyl groups in component (A). The resulting composition will not evidence a thorough cure at values below 0.4. Bubbles may appear in the ultimately obtained silicone rubber when this ratio has a value in excess of 10.

35

35 The organohydrogenpolysiloxane (D) imparts good adherence to the low-temperature cured silicone rubber and, like component (C), also functions to cure the present composition. Component (D) has the following general formula



55 and contains at least two silicon-bonded hydrogen atoms in each molecule.  $\text{R}^1$  therein represents monovalent hydrocarbon groups, excluding alkenyl groups, and is exemplified by the same groups given above.  $\text{R}^2$  represents the hydrogen atom and monovalent hydrocarbon groups excluding alkenyl groups also as elaborated above. The subscript  $x$  is a positive integer whose value preferably is from 5 to 1,000, and more preferably is from 5 to 100. The viscosity of component (D) at 25°C is preferably from 3 to 10,000 mPa.s (centipoise) and more preferably is from 3 to 300 mPa.s (centipoise). Organohydrogenpolysiloxane (D) is exemplified by trimethylsiloxo-endblocked methylhydrogenpolysi-

loxanes and dimethylhydrogensiloxyl-endblocked methylhydrogenpolysiloxanes. These organohydrogenpolysiloxanes may be used singly or in combinations of two or more.

Component (D) is added in a quantity that affords a value from 0.01 to 0.5, and preferably from 0.05 to 0.4 for the molar ratio of silicon-bonded hydrogen atom in component (D) to alkenyl group in component (A). A satisfactory adherence cannot be imparted when this molar ratio is below 0.01. When this ratio exceeds 0.5, the ultimately obtained silicone rubber will exhibit a very large durometer, which will typically make the rubber undesirable for use in FFRs.

The platinum catalyst (E) accelerates the cure of the subject composition. Catalyst (E) is exemplified by platinum black; supported catalysts like platinum-on-alumina, platinum-on-silica and platinum-on-carbon; chloroplatinic acid or alcohol solutions of chloroplatinic acid; platinum/olefin complexes; platinum/vinylsiloxane complexes; and by encapsulated platinum catalyst contained in a thermoplastic organic resin such as a methyl methacrylate resin, polycarbonate resin, polystyrene resin and silicone resin.

Component (E) is added in a catalytic quantity and may be added in any quantity sufficient to cure the claimed composition. In specific terms, the addition of component (E) preferably provides from 0.01 to 500 weight parts, and more preferably from 0.1 to 100 weight parts of platinum metal in component (E) for each one million weight of parts component (A).

A curing inhibitor can be added to our composition on an optional basis to improve the composition's storage stability and/or its handling characteristics. The curing inhibitor is exemplified by acetylenic compounds such as 3-methyl-1-butyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol and 3-phenyl-1-butyn-3-ol; ene-yne compounds such as 3-methyl-3-penten-1-yne or 3,5-dimethyl-3-hexen-1-yne; 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane; 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane; triazoles such as benzotriazole; phosphines; mercaptans; hydrazines; and so forth. The curing inhibitor is preferably added at from 0.001 to 5 weight parts per 100 weight parts of component (A).

To adjust the durometer of the ultimately obtained silicone rubber, the present composition preferably contains as an optional component of diorganopolysiloxane that contains neither Si-bonded alkenyl nor Si-bonded hydrogen. The Si-bonded groups in such a diorganopolysiloxane are exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, pentyl and hexyl; aryl groups such as phenyl, tolyl and xylyl; aralkyl groups such as benzyl or phenethyl; haloalkyl groups such as 3-chloropropyl or 3,3,3-trifluoropropyl; alkoxy groups such as methoxy or ethoxy and hydroxyl group. The methyl group is preferred. To obtain good handling characteristics for the corresponding silicone rubber composition and to fabricate high-quality fluororesin-covered fixing rolls, the viscosity of this diorganopolysiloxane at 25°C is preferably at least 100 mPa.s (centipoise) and particularly preferably is from 1,000 to 10,000,000 mPa.s (centipoise). The subject diorganopolysiloxane is exemplified by trimethylsiloxy-endblocked dimethylpolysiloxanes, trimethylsiloxy-endblocked dimethylsiloxane-methylphenylsiloxane copolymers, trimethylsiloxy-endblocked dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers, silanol-endblocked dimethylpolysiloxanes, silanol-endblocked dimethylsiloxane-methylphenylsiloxane copolymers, and silanol-endblocked dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers. These diorganopolysiloxanes may be used singly or as combinations of two or more. To adequately reduce the durometer of the silicone rubber, while also avoiding bleed out by this component from the silicone rubber, the diorganopolysiloxane is added at from 5 to 100 weight of parts, and preferably at from 10 to 50 weight of parts per 100 weight parts of component (A).

To further reduce the compression set of our silicone rubber composition, it will preferably contain a very small amount of a six-member ring compound having an unsaturated carbon-nitrogen bond in the ring, for example, pyridine, pyrazine, pyrimidine, and 1,3,5-triazine, or the derivative of such a compound. The usual pigments, heat stabilizers, flame retardants, and the like may be introduced into the present composition on an optional basis within a range that does not impair the objects of the present invention.

Our composition is prepared by mixing components (A) to (E), and any optional components, to homogeneity. The method for preparing the composition is exemplified by mixing the components (A) to (E), and any optional components, to homogeneity in any known mixing device such as a 2-roll mill, kneader mixer, or a "ROSS®" mixer, available from the Charles Ross & Sons Company of Hauppauge, NY.

The fluororesin-covered fixing roll of the present invention is explained below.

#### Reference numbers

1	roll shaft
2	silicone rubber layer
3	fluororesin layer

As shown in Figure 1, our FFR is defined by the presence of a fluororesin layer 3 on the circumference of a roll shaft 1 with a silicone rubber layer 2 interposed between the fluororesin layer and the roll shaft wherein said silicone

rubber layer 2 is formed by the cure of the aforementioned silicone rubber composition. The technique for fabricating a fixing roll according to the present invention is exemplified by mounting a metal roll shaft, e.g., of iron or aluminum, in a mold designed for roll fabrication, installing a fluororesin tube along the interior wall of the mold, injecting the silicone rubber composition into the cavity between the roll shaft and the fluororesin tube, and finally curing the silicone rubber composition. The fluororesin has a thickness of no more than 0.1 mm, and preferably has a thickness within the range from 0.1 to 50 micrometers. The fluororesin is itself exemplified by polytetrafluoroethylene resins (PTFE), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer resins (PFA), fluorinated ethylene-propylene copolymer resins (FEP), ethylene-tetrafluoroethylene copolymer resins (ETFE), polychlorotrifluoroethylene copolymer resins (PCTFE), polyvinylidene fluoride resins (PVDF), polyvinyl fluoride resins (PVF), ethylenechlorotrifluoroethylene copolymer resins (ECTFE), and tetrafluoroethylenehexafluoropropylene copolymer resins (FEP). The silicone rubber layer preferably has a thickness of 2 to 30 mm. The circumference of the roll shaft is preferably treated with primer to obtain additional adherence between the roll shaft and the silicone rubber layer. The compression molders, transfer molders, and injection molders ordinarily used for molding liquid silicone rubber compositions can be used for the pressurized introduction of our silicone rubber composition into the cavity between the roll shaft and fluororesin tube.

A very low curing temperature for the silicone rubber composition results in a slow cure rate and thus a substantially reduced productivity for fabrication of FFRs. On the other hand, a very high curing temperature causes the development of creases in the surface of the resulting FFR. As a result of these considerations, the curing temperature is preferably from 70°C to 140°C, and particularly preferably from 90°C to 120°C. An additional heat treatment at 150°C to 250°C is preferred for obtaining additional reductions in the compression set of our silicone rubber afforded by low-temperature cure. This heat treatment will not cause creasing in the surface of the FFR because our silicone rubber has a smaller coefficient of thermal expansion than the uncured composition. Our FFR is highly reliable, and good adherence between the roll shaft and the silicone rubber layer make it ideal for use as a fixing roll in electrophotographic copiers, printers, and facsimile machines.

## 25 Examples

The FFR silicone rubber composition and FFR of the present invention will be explained in greater detail through working examples. The viscosity values reported in the examples were measured at 25°C. The silicone rubbers were evaluated by the following methods.

### 30 Durometer

The silicone rubber composition was cured in a hot press at 120°C for 30 minutes to yield a silicone rubber, which was then additionally heated in an oven at 200°C for 4 hours. The durometer of the resulting silicone rubber was measured using the JIS A hardness meter specified in JIS K 6301.

### 35 Compression set

The silicone rubber composition was cured in a hot press at 120°C for 30 minutes to yield a silicone rubber, which was then additionally heated in an oven at 200°C for 4 hours. The compression set of the resulting silicone rubber was measured using the compression set test method specified in JIS K 6301. The heating temperature during the compression test was 180°C and the heating time was 22 hours.

### 40 Adherence

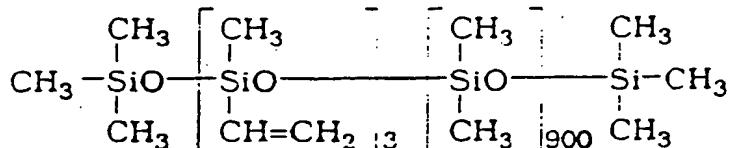
A commercial primer was uniformly coated on the surface of an aluminum test panel and was then thoroughly dried by holding in an oven for 30 minutes at 150°C. Next a silicone rubber composition was coated onto the treated test panel and cured for 30 minutes with a hot press at 100°C to yield a silicone rubber adhered to the panel. The silicone rubber was then peeled from the test panel surface at a 90° angle, and the proportion of the area of cohesive failure by the silicone rubber in the overall area of adhesion was determined (% cohesive failure). The % cohesive failure was similarly determined for a curing temperature of 150°C.

### 45 Volume resistivity

The volume resistivity of our silicone rubber composition, prepared as described above, was measured according to the volume resistivity test method specified in JIS C 2123.

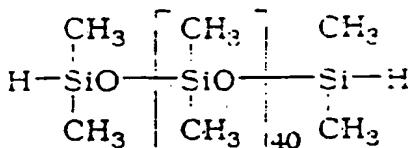
Example 1

Using a "ROSS®" mixer, 100 weight parts of trimethylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane copolymer (viscosity = 40,000 mPa.s [centipoise], vinyl content = 0.12 weight%) with the formula



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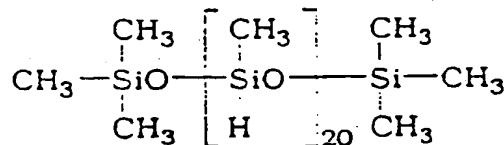
and 30 weight parts of crushed quartz, with an average particle size of 5 micrometers, were mixed to homogeneity. The following were then mixed to homogeneity into the mixture thus prepared to yield a silicone rubber composition: 15 6 weight parts of dimethylhydrogensiloxy-endblocked dimethylpolysiloxane (viscosity = mPa.s [38 centipoise], silicon-bonded hydrogen content = 0.065 weight%) with the formula



25

thereby giving a value of 0.9 for the molar ratio of silicon-bonded hydrogen atom in this dimethylpolysiloxane to the vinyl group in the above methylvinylsiloxane-dimethylsiloxane copolymer; 0.06 weight part of trimethylsiloxy-end-blocked methylhydrogenpolysiloxane (viscosity = 20 mPa.s [centipoise], silicon-bonded hydrogen content = 1.47 weight%) with the formula

30



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thereby giving a value of 0.2 for the molar ratio of silicon-bonded hydrogen atom in this methylhydrogenpolysiloxane to vinyl group in the methylvinylsiloxane-dimethylsiloxane copolymer; and 0.5 weight part of isopropanolic chloroplatinic acid solution (content of platinum metal = 1 weight%).

The silicone rubber afforded by the cure of this silicone rubber composition had a durometer (JIS A) of 7 and a compression set of 5%. This silicone rubber gave 100% cohesive failure at both curing temperatures (100°C and 150°C).

45

Commercial primer was uniformly coated on the circumference of an iron cylindrical roll shaft with a diameter of 10 mm, and the primer was thoroughly dried by holding in an oven at 150°C for 30 minutes. Commercial primer was also uniformly coated on the interior wall of a tube of tetrafluoroethyleneperfluoroalkyl perfluorovinyl ether copolymer (film thickness = 50 micrometers) whose interior wall had also been preliminarily treated with alkali. The primer was thoroughly dried by then holding the tube for 1 hour at room temperature. The roll shaft was thereafter mounted in a mold designed for roll fabrication, and the tube was installed along the interior wall of the mold. The above silicone rubber composition was subsequently injected into the cavity between the roll shaft and tube and was cured at 100°C for 30 minutes to yield a FFR with a covering thickness of 10 mm. Inspection of the fixing roll surface found it to be free of creases or wrinkles, while evaluation of the adherence between the roll shaft and silicone rubber layer determined this adherence to be excellent. Creasing still did not appear in the surface of this fixing roll when it was subsequently heated for 4 hours in an oven at 200°C.

55

This fixing roll was installed in an electrophotographic copier and 150,000 copies were continuously run off on A4 copy paper. No paper creasing or paper jams occurred, and the image was clearly copied.

Comparative Example 1

A silicone rubber composition was prepared as in Example 1, but in this case omitting the trimethylsiloxy-end-blocked methylhydrogenpolysiloxane that was used in Example 1.

This silicone rubber composition cured into a silicone rubber with a durometer (JIS A) of 6 and a compression set of 5%. This silicone rubber gave 20% cohesive failure at a curing temperature of 100°C, and 100% cohesive failure at a curing temperature of 150°C.

This silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing, but a partial delamination was observed at the interface between the roll shaft and the silicone rubber layer.

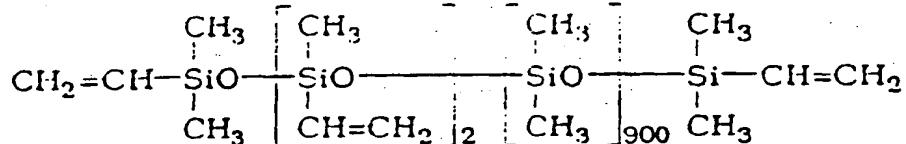
Comparative Example 2

A silicone rubber composition was prepared as in Example 1, but in this case the addition of the trimethylsiloxy-endblocked methylhydrogenpolysiloxane was increased to 0.3 weight part, thereby giving a value of 1.0 for the molar ratio of silicon-bonded hydrogen atom in this methylhydrogenpolysiloxane to the vinyl group in the methylvinylsiloxane-dimethylsiloxane copolymer.

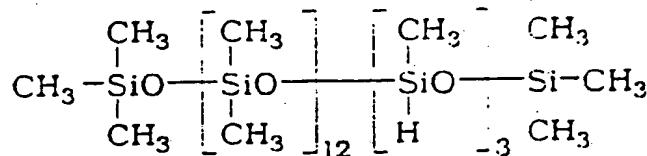
This silicone rubber composition cured into a silicone rubber with a durometer (JIS A) of 20, thus confirming a substantial increase in this property.

Example 2

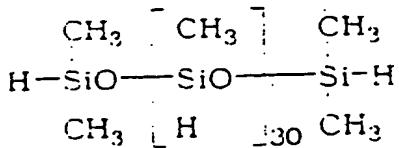
Using a "ROSS®" mixer, 100 weight parts of dimethylvinylsiloxane-endblocked methylvinylsiloxane-dimethylsiloxane copolymer (viscosity = 40,000 mPa.s [centipoise], vinyl content = 0.16 weight%) with the formula



15 weight parts of crushed quartz, with an average particle size of 5 micrometers, and 8 weight parts of carbon black ("DENKA®" Acetylene Black) were mixed to homogeneity. "DENKA®" is available from Denki Kagaku Kogyo Kabushiki Kaisha of Tokyo, Japan. The following were then mixed to homogeneity into the mixture to yield a silicone rubber composition: 5 weight parts of trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 10 mPa.s [centipoise], silicon-bonded hydrogen content = 0.24 weight%) with the formula



50 thereby giving a value of 2.0 for the molar ratio of silicon-bonded hydrogen atom in this dimethylsiloxane-methylhydrogensiloxane copolymer to the vinyl group in the methylvinylsiloxane-dimethylsiloxane copolymer, 0.04 weight part of dimethylhydrogensiloxane-endblocked methylhydrogenpolysiloxane (viscosity = 30 mPa.s [centipoise], silicon-bonded hydrogen content = 1.65 weight%) with the formula



10 thereby giving a value of 0.11 for the molar ratio of silicon-bonded hydrogen atom in this methylhydrogenpolysiloxane to vinyl group in the methylvinylsiloxane-dimethylsiloxane copolymer; and 0.5 weight part of isopropanolic chloroplatinic acid solution (content of platinum metal = 1 weight%).

15 The silicone rubber afforded by cure of this silicone rubber composition had a durometer (JIS A) of 12, a volume resistivity of  $1 \times 10^4$  ohm-cm, and a compression set of 8%. This silicone rubber gave 100% cohesive failure at both curing temperatures (100°C and 150°C).

20 The silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. Moreover, the adherence between the roll shaft and silicone rubber layer was excellent. Creasing still did not appear in the surface of this fixing roll when it was subsequently heated for 4 hours at 200°C.

25 This fixing roll was installed in an electrophotographic copier and 150,000 copies were continuously run off on A4 copy paper. No paper creasing or paper jams occurred, and the image was clearly copied.

#### Comparative Example 3

30 A silicone rubber composition was prepared as in Example 2, but without using the dimethylhydrogensiloxy-end-blocked methylhydrogenpolysiloxane of Example 2.

35 The silicone rubber afforded by cure of this silicone rubber composition had a durometer (JIS A) of 11, a volume resistivity of  $1 \times 10^4$  ohm-cm, and a compression set of 8%. This silicone rubber gave 50% cohesive failure at a curing temperature of 100°C, and 100% cohesive failure at a curing temperature of 150°C.

40 This silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. However, partial delamination was observed at the interface between the roll shaft and silicone rubber layer.

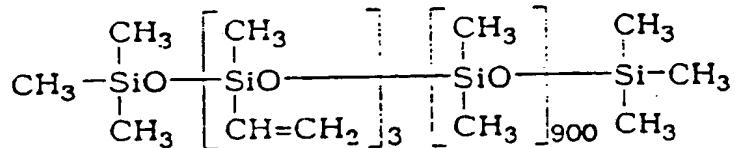
#### Comparative Example 4

45 A silicone rubber composition was prepared as in Example 2, but in this case the amount of dimethylhydrogensiloxy-endblocked methylhydrogenpolysiloxane was 0.4 weight parts. This gave a value of 1.1 for the molar ratio of silicon-bonded hydrogen atom in this methylhydrogenpolysiloxane to the vinyl group in the methylvinylsiloxane-dimethylsiloxane copolymer.

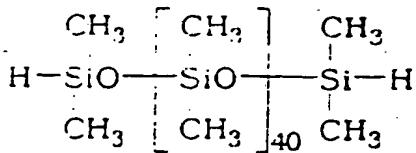
50 This silicone rubber composition cured into a silicone rubber with a durometer (JIS A) of 25, thus confirming a substantial increase in this property.

#### Example 3

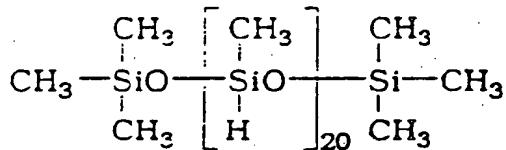
55 Using a "ROSS®" mixer, 100 weight parts of trimethylsiloxy-endblocked methylvinylsiloxane-dimethylsiloxane copolymer (viscosity = 40,000 mPa.s [centipoise], vinyl content = 0.12 weight%) with the formula



55 and 90 weight parts crushed quartz with an average particle size of 5 micrometers were mixed to homogeneity. The following were then mixed to homogeneity into the above mixture to yield a silicone rubber composition: 20 weight parts of trimethylsiloxy-endblocked dimethylpolysiloxane with a viscosity of 100,000 mPa.s [centipoise]; 6 weight parts of dimethylhydrogensiloxy-endblocked dimethylpolysiloxane (viscosity = 38 mPa.s [centipoise] silicon-bonded hydrogen content = 0.065 weight%) with the formula



10 thereby giving a value of 0.9 for the molar ratio of silicon-bonded hydrogen atom in this dimethylpolysiloxane to the vinyl group in the above methylvinylsiloxane-dimethylsiloxane copolymer; 0.1 weight part of trimethylsiloxy-endblocked methylhydrogenpolysiloxane (viscosity = 20 mPa.s [centipoise], silicon-bonded hydrogen content = 1.47 weight%) with the formula



20 thereby giving a value of 0.3 for the molar ratio of silicon-bonded hydrogen in this methylhydrogenpolysiloxane to vinyl in the above methylvinylsiloxane-dimethylsiloxane copolymer; and 0.5 weight part isopropanolic chloroplatinic acid solution (content of platinum metal = 1 weight%).

25 The silicone rubber afforded by cure of this silicone rubber composition had a durometer (JIS A) of 10 and a compression set of 5%. This silicone rubber gave 100% cohesive failure at both curing temperatures (100°C and 150°C).

30 The silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. Moreover, the adherence between the roll shaft and silicone rubber layer was excellent. Creasing still did not appear in the surface of this fixing roll when it was subsequently heated for 4 hours at 200°C.

35 This fixing roll was installed in an electrophotographic copier and 150,000 copies were continuously run off on A4 copy paper. No paper creasing or paper jams occurred, and the image was clearly copied.

### 35 Comparative Example 5

A silicone rubber composition was prepared as in Example 3, but without using the trimethylsiloxy-endblocked methylhydrogenpolysiloxane of Example 3.

40 The silicone rubber afforded by cure of this silicone rubber composition had a durometer (JIS A) of 9 and a compression set of 5%. This silicone rubber gave 20% cohesive failure at a curing temperature of 100°C and 100% cohesive failure at a curing temperature of 150°C.

45 This silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. However, partial delamination was observed at the interface between the roll shaft and the silicone rubber layer.

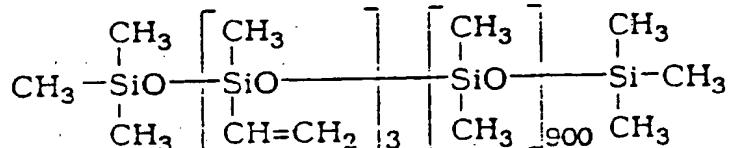
### 45 Comparative Example 6

50 A silicone rubber composition was prepared as in Example 3, but in this case adding 2 weight parts of the dimethylhydrogensiloxy-endblocked dimethylpolysiloxane of Example 3, thereby giving a value of 0.3 for the molar ratio of silicon-bonded hydrogen in this dimethylpolysiloxane to the vinyl in the methylvinylsiloxane-dimethylsiloxane copolymer, and adding 0.3 weight part of the trimethylsiloxy-endblocked methylhydrogenpolysiloxane, thereby giving a value of 0.9 for the molar ratio of silicon-bonded hydrogen in this methylhydrogenpolysiloxane to the vinyl in the methylvinylsiloxane-dimethylsiloxane copolymer.

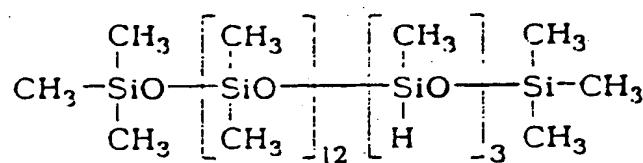
55 This silicone rubber composition cured into a silicone rubber with a durometer (JIS A) of 25, thus confirming a substantial increase in this property.

Example 4

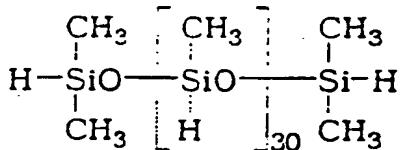
Using a "ROSS®" mixer, 100 weight parts of dimethylvinylsiloxane-endblocked methylvinylsiloxane-dimethylsiloxane copolymer (viscosity = 40,000 mPa.s [centipoise], vinyl content = 0.16 weight%) with the formula



10 30 weight parts of crushed quartz with an average particle size of 5 micrometers, and 8 weight parts of carbon black ("DENKA®" Acetylene Black) were mixed to homogeneity. The following were then mixed to homogeneity into the mixture thus prepared to yield a silicone rubber composition: 20 weight parts of trimethylsiloxane-endblocked dimethylpolysiloxane with a viscosity of 300,000 mPa.s [centipoise], 4 weight parts of trimethylsiloxane-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 10 mPa.s [centipoise], silicon-bonded hydrogen content = 0.24 weight%) with the formula



20 25 thereby giving a value of 1.7 for the molar ratio of silicon-bonded hydrogen in this dimethylsiloxane-methylhydrogen-siloxane copolymer to the vinyl in the methylvinylsiloxane-dimethylsiloxane copolymer; 0.05 weight part of dimethylhydrogensiloxane-endblocked methylhydrogenpolysiloxane (viscosity = 30 mPa.s [centipoise], silicon-bonded hydrogen content = 1.65 weight%) with the formula



35 40 thereby giving a value of 0.14 for the molar ratio of silicon-bonded hydrogen in this methylhydrogenpolysiloxane to vinyl in the methylvinylsiloxane-dimethylsiloxane copolymer; and 0.5 weight part of isopropanolic chloroplatinic acid solution (content of platinum metal = 1 weight%).

45 The silicone rubber afforded by the cure of this silicone rubber composition had a durometer (JIS A) of 15, a volume resistivity of  $1 \times 10^4$  ohm-cm, and a compression set of 8%. This silicone rubber gave 100% cohesive failure at both curing temperatures (100°C and 150°C).

50 This silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. Moreover, the adherence between the roll shaft and silicone rubber layer was excellent. Creasing still did not appear in the surface of this fixing roll when it was subsequently heated for 4 hours at 200°C.

This fixing roll was installed in an electrophotographic copier and 150,000 copies were continuously run off on A4 copy paper. No paper creasing or paper jams occurred, and the image was clearly copied.

Comparative Example 7

55 A silicone rubber composition was prepared as in Example 4, but in this case without the dimethylhydrogensiloxane-endblocked methylhydrogenpolysiloxane of Example 4.

The silicone rubber afforded by cure of this silicone rubber composition had a durometer (JIS A) of 14, a volume resistivity of  $1 \times 10^4$  ohm-cm, and a compression set of 8%. This silicone rubber gave 50% cohesive failure at a curing temperature of 100°C, and 100% cohesive failure at a curing temperature of 150°C.

This silicone rubber composition was also used to fabricate a FFR as in Example 1. This fixing roll, which was fabricated by curing for 30 minutes at 100°C, did not evidence surface creasing. However, partial delamination was observed at the interface between the roll shaft and the silicone rubber layer.

For purposes of comparison, a FFR was fabricated by curing at 150°C for 30 minutes. Creasing was observed on the surface of this fixing roll.

Even when cured at the relatively low temperatures necessary to avoid the development of wrinkles or creases in the surface of FFRs, the FFR silicone rubber composition of the present invention is surprisingly able to form a silicone rubber with a low compression set and an excellent adherence to the roll shaft. The present invention also provides a highly reliable fluororesin-covered fixing roll through the use of this silicone rubber composition in fixing roll fabrication.

## 15 Claims

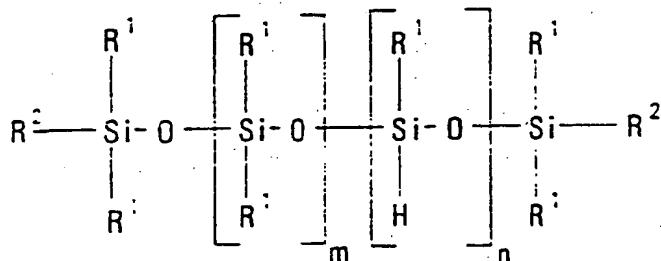
### 1. A silicone rubber composition comprising:

(A) 100 parts by weight of a diorganopolysiloxane having an average of at least two silicon-bonded alkenyl groups per molecule and containing an average at least 0.5 silicon-bonded alkenyl groups per molecule in pendant positions on the molecular chain:

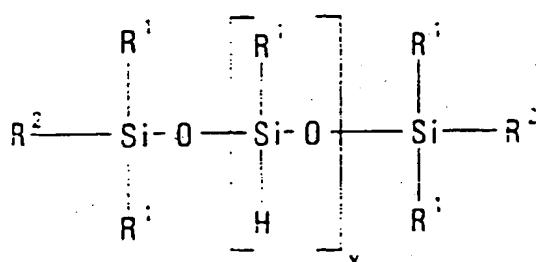
(B) 5 to 100 parts by weight of a filler;

(C) an organopolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, in a quantity that affords a value from 0.4 to 10 for the molar ratio of silicon-bonded hydrogen atoms in component

(C) to alkenyl groups in component (A), said organopolysiloxane having the general formula



(D) an organohydrogenpolysiloxane with the general formula



50

said organohydrogenpolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule, in a quantity that affords a value from 0.01 to 0.5 for the molar ratio of silicon-bonded hydrogen atoms in component (D) to alkenyl groups in component (A); and

55

(E) a catalytic quantity of platinum catalyst;

wherein  $R^1$  is a monovalent hydrocarbon group,  $R^2$  is a hydrogen atom or a monovalent hydrocarbon group,  $m$  is a positive integer,  $n$  is an integer with a value of zero or greater,  $x$  is a positive integer, and both the organopolysiloxane and the organohydrogenpolysiloxane are free of alkenyl groups.

2. The silicone rubber composition of claim 1 wherein the silicon-bonded alkenyl groups of component (A) are individually selected from the group consisting of vinyl, alkyl, butenyl, pentenyl, hexenyl and heptenyl.

5 3. The silicone rubber composition according to claim 1 or claim 2 wherein the viscosity at 25°C of component (A) is 1,000 to 1,000,000 mPa.s (centipoise).

4. The silicone rubber composition according to any of claims 1 to 3 wherein R<sup>1</sup> is individually selected from the group consisting of alkyl groups, aryl groups, aralkyl groups and haloalkyl groups.

10 5. The silicone rubber composition according to any of claims 1 to 4 wherein R<sup>2</sup> is individually selected from the group consisting of hydrogen atoms, alkyl groups, aryl groups, aralkyl groups and haloalkyl groups.

6. The silicone rubber composition according to any of claims 1 to 5 wherein the viscosity at 25°C of component (C) is 3 to 10,000 mPa.s (centipoise).

15 7. The silicone rubber composition according to any of claims 1 to 6 wherein the viscosity at 25°C of component (D) is 3 to 10,000 mPa.s (centipoise).

8. A method of producing a FFR comprising the steps of:

20 (i) placing a roll shaft in a mold;  
(ii) installing a fluororesin tube along the interior wall of the mold;  
(iii) injecting the silicone rubber composition of any of claims 1 to 7 into the cavity between the roll shaft and the fluororesin tube.

25 9. The method of claim 8 wherein the cure of said silicone rubber composition occurs at a temperature of 70°C to 140°C.

10. The method of claim 9 the silicone rubber layer has a thickness of 2 to 30 mm.

30 11. The method according to any of claims 8 to 10 further comprising the step of  
(v) exposing the cured silicone rubber to heat treatment of 150°C to 250°C.

12. An FFR obtainable by a method according to any of claims 8 to 11.

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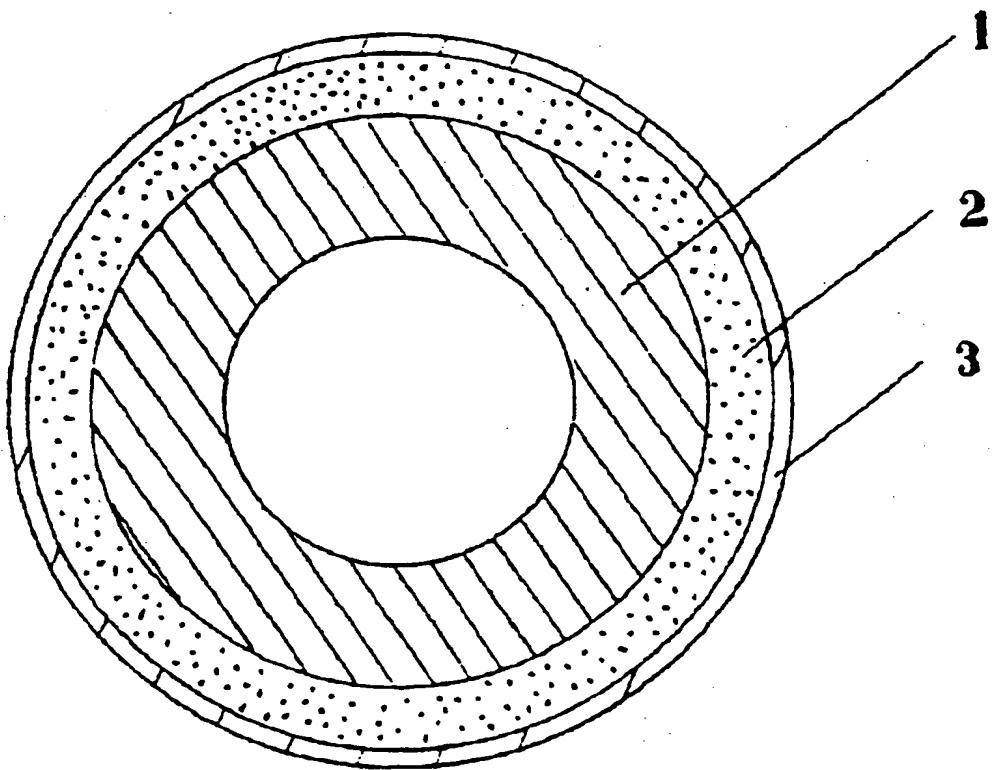
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Figure 1.





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• Ushio, Yoshito, c/o Dow Corning  
Ichihara-shi, Chiba Pref. (JP)

(30) Priority: 13.09.1995 JP 260851/95

(74) Representative: Dowden, Marina  
Elkington and Fife  
Prospect House,  
8 Pembroke Road  
Sevenoaks, Kent TN13 1XR (GB)

(71) Applicant: Dow Corning Toray Silicone Company  
Limited  
Tokyo (JP)

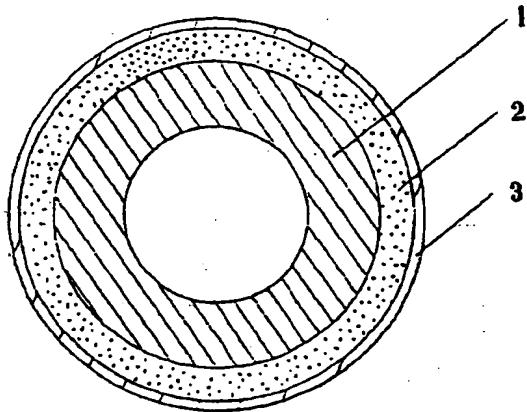
(72) Inventors:  
• Nakamura, Akito, c/o Dow Corning  
Ichihara-shi, Chiba Pref. (JP)

(54) **Silicone rubber composition for fluororesin-covered fixing rolls and fluororesin-covered fixing rolls**

(57) Silicone rubber composition comprising an alkenyl-substituted diorganopolysiloxane, an inorganic filler, an organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, in a quantity that affords a value from 0.4 to 10 for the molar ratio of silicon-bonded hydrogen in the organopolysiloxane to alkenyl groups in the alkenyl-substituted diorganopolysiloxane, an organohydrogenpolysiloxane, in a quantity that affords a value from 0.01 to 0.5 for the molar ratio of silicon-bonded hydrogen in this component to alkenyl groups in the alkenyl-substituted diorganopolysiloxane, and a platinum catalyst.

A fluororesin-covered fixing roll in which a fluororesin layer is placed over the circumference of a roll shaft with a silicone rubber layer interposed between the fluororesin layer and the roll shaft, wherein said silicone rubber composition is formed by curing the silicone rubber composition described above.

Figure 1.





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 96 30 6663

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
X	EP 0 517 524 A (SHIN-ETSU) * page 2, line 22 - line 41 * * examples * * claims * -----	1-12	C08L83/04 G03G15/20						
A	US 5 223 344 A (C. A. SUMPTER ET AL.) * column 1, line 5 - line 13 * * column 5, line 19 - line 28 * * column 5, line 41 - line 42 * * column 5, line 49 - line 50 * * claims 1,19 * -----	1-7							
			TECHNICAL FIELDS SEARCHED (Int.Cl.)						
			C08L G03G						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>BERLIN</td> <td>4 August 1997</td> <td>Hoepfner, W.</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	BERLIN	4 August 1997	Hoepfner, W.
Place of search	Date of completion of the search	Examiner							
BERLIN	4 August 1997	Hoepfner, W.							
<p>CATEGORY OF CITED DOCUMENTS</p> <table border="0" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top;">           X : particularly relevant if taken alone            Y : particularly relevant if combined with another document of the same category            A : technological background            O : non-written disclosure            P : intermediate document         </td> <td style="width: 50%; vertical-align: top;">           T : theory or principle underlying the invention            E : earlier patent document, but published on, or after the filing date            D : document cited in the application            L : document cited for other reasons            &amp; : member of the same patent family, corresponding document         </td> </tr> </table>				X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document				
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